Föster Resonance Energy Transfer(FRET)

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April 16, 2024

1 step one

The formula for Fermi's golden rule is

$$\omega_{fi} = \frac{2\pi}{\hbar}|V_{fi}|^2\delta(\omega_f - \omega_i) \tag{1}$$

2 step two

The total Hamiltonian is

$$H = H_D + H_A + V_{DA} \tag{2}$$

3 step three

V_{DA} can be written as the following form

$$V_{DA} = \sum_i \sum_a \frac{Z_i Z_a}{|R_i^D - R_a^A|} = \sum_i \sum_a \frac{Z_i Z_a}{r_D + r_{D\to i} - (r_A + r_{A\to a})} = \sum_i \sum_a \frac{Z_i Z_a}{r_{DA} + r_{D\to i} - r_{A\to a}} \tag{3}$$

where, we define $r_{DA} = \vec{R}, r_{A\to a} - r_{D\to i} = \vec{r}$

Use Taylor expansion to calculate the following formula

$$\frac{1}{\sqrt{(\vec{R}-\vec{r})(\vec{R}-\vec{r})}} = \frac{1}{\sqrt{\vec{R}^2 + \vec{r}^2 - 2\vec{R}\vec{r}}} = \frac{1}{R}\frac{1}{\sqrt{1 + (\frac{\vec{r}}{\vec{R}})^2 - \frac{2\vec{R}\vec{r}}{\vec{R}^2}}} \tag{4}$$

Let $x = (\frac{\vec{r}}{\vec{R}})^2 - \frac{2\vec{R}\vec{r}}{\vec{R}^2}$, perform Taylor expansion at $x_0 = 0$, retaining only first-order and second-order terms. The above formula is approximately equal to

$$\frac{1}{R}(-\frac{1}{2} - \frac{\hat{R}\vec{r}}{R} - \frac{1}{2}\frac{r^2}{R^2} + \frac{3}{2}\frac{\hat{R}\cdot\vec{r}\vec{r}\cdot\hat{R}}{R^2}) \tag{5}$$

where, $\hat{R} = \frac{\vec{R}}{R}$, $\vec{r}\vec{r} = (\tilde{r}_{D\to i} - \tilde{r}_{A\to a})^2 = \tilde{r}^2_{D\to i} + \tilde{r}^2_{A\to a} - 2\tilde{r}_{D\to i}\cdot\tilde{r}_{A\to a}$

Substitute formula 5 into formula 3

$$\begin{aligned}
&\sum_i \sum_a Z_i Z_a \frac{1}{R}(-\frac{1}{2} - \frac{\hat{R}\vec{r}}{R} - \frac{1}{2}\frac{r^2}{R^2} + \frac{3}{2}\frac{\hat{R}\cdot\vec{r}\vec{r}\cdot\hat{R}}{R^2}) \\
&= \sum_i \sum_a Z_i Z_a (-\frac{1}{2}\frac{r^2}{R^3} + \frac{3}{2}\frac{\hat{R}\cdot\vec{r}\vec{r}\cdot\hat{R}}{R^3}) \\
&= \sum_i \sum_a Z_i Z_a (\frac{\tilde{r}_{D\to i}\tilde{r}_{A\to a}}{R^3} - 3\frac{\hat{R}\cdot\tilde{r}_{D\to i}\tilde{r}_{A\to a}\cdot\hat{R}}{R^3}) \\
&= \frac{\sum_i Z_i\tilde{r}_{D\to i}\sum_a Z_a\tilde{r}_{A\to a}}{R^3} - \frac{3(\sum_i Z_i\tilde{r}_{D\to i}\hat{R})(\sum_a Z_a\tilde{r}_{A\to a}\hat{R})}{R^3} \\
&= \frac{\vec{\mu}_D\cdot\vec{\mu}_A - 3(\vec{\mu}_D\cdot\hat{R})(\vec{\mu}_A\cdot\hat{R})}{R^3}
\end{aligned} \tag{6}$$

4 step four

We write the transition dipole matrix elements that couple the ground and excited electronic states for the donor and acceptor as

$$\vec{\mu}_A = |A\rangle \vec{\mu}_{AA^*} \langle A^*| + \langle A^*| \vec{\mu}_{A^*A} |A\rangle \tag{7}$$

$$\vec{\mu}_D = |D\rangle \vec{\mu}_{DD^*} \langle D^*| + \langle D^*| \vec{\mu}_{D^*D} |D\rangle \tag{8}$$

For the dipole operator, we can separate the scalar and orientational contributions as $\vec{\mu}_A = \hat{\mu_A}\mu_A$ This allows the transition dipole interaction in fomula 6 to be written as

$$V = \mu_A\mu_D \frac{\kappa}{R^3}[|D^*A\rangle \langle A^*D| + |A^*D\rangle \langle D^*A|] \tag{9}$$

All of the orientational factors are now in the term κ

$$\kappa = \hat{\mu}_D \cdot \hat{\mu}_A - 3(\hat{\mu}_D \cdot \hat{R})(\hat{\mu}_A \cdot \hat{R}) \tag{10}$$

We can now obtain the rates of energy transfer using Fermi's Golden Rule expressed as a correlation function in the interaction Hamiltonian:

$$\begin{aligned}
\omega_{if} =& \frac{2\pi}{\hbar}|V_{if}|^2\delta(\omega_i - \omega_f) \\
=& \frac{2\pi}{\hbar}| \langle i| V |f\rangle |^2\delta(\omega_i - \omega_f) \\
=& \frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt e^{\frac{i}{\hbar}(\omega_i-\omega_f)} \langle i| \hat{V} |f\rangle \langle f| \hat{V} |i\rangle \\
=& \frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt \langle i| e^{\frac{i}{\hbar}\hat{H}_0 t}\hat{V}e^{-\frac{i}{\hbar}\hat{H}_0 t} |f\rangle \langle f| \hat{V} |i\rangle \\
=& \frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt \langle i| \hat{V}(t) |f\rangle \langle f| \hat{V} |i\rangle \\
=& \frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt\langle \hat{V}(t)\hat{V}(0)\rangle
\end{aligned} \tag{11}$$

where, $2\pi\delta(\omega_i - \omega_f) = \frac{1}{\hbar}\int_{-\infty}^{\infty} dte^{(i(\omega_i-\omega_f)t/\hbar)}$ and $E_k |k\rangle = \hat{H}_0 |k\rangle$ $(k = i, f)$

Thus, fomula 11 can be written in

$$\omega_{ET} = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt \frac{\langle\kappa^2\rangle}{r^6} \langle D^*A| \mu_D(t)\mu_A(t)\mu_D(0)\mu_A(0) |D^*A\rangle \tag{12}$$

$$= \frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt \frac{\langle\kappa^2\rangle}{r^6} \langle D^*| \mu_D(t)\mu_D(0) |D\rangle \langle A| \mu_A(t)\mu_A(0) |A^*\rangle \tag{13}$$

$$= \frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt \frac{\langle\kappa^2\rangle}{r^6} \int_{-\infty}^{\infty} d\omega\delta_{abs}^A(\omega)\delta_{emi}^A(\omega) \tag{14}$$

where, $\int_{-\infty}^{\infty} d\omega\delta_{abs}^A(\omega)\delta_{emi}^A(\omega)$ is the overlap between donor emission spectrum and acceptor absorption spectrum.